Bimetallic Pt–Au Colloids as Catalysts for Photochemical Dehydrogenation

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Bimetallic colloidal particles, consisting of variable mole fractions of Pt and Au, catalyse H_2 formation from sacrificial photosystems and as the fraction of Au increases there is a substantial decrease in the rate of hydrogenation of the reactants such that higher yields of H_2 are attainable.

Colloidal dispersions of noble metals, notably Pt, have been used as catalysts for the reduction of protons to H_2 under photolytic and radiolytic conditions,[1] ostensibly with a view to storing solar energy in the form of chemical potential.[2] Although extremely efficient for short irradiation periods these colloids are non-specific for H_2 formation. Indeed, as H_2 accumulates in the system the colloids catalyse hydrogenation of unsaturated bonds.[3] The total yield of H_2 attainable from any such photosystem is limited, therefore, by the susceptibility of the reactants to hydrogenation and reduction. Often, the

Table 1. Influence of the composition of the $Pt_{100-x}Au_x$ colloidal particles on the rates and total yields for H_2 evolution and for hydrogenation of particular reactants for the two photosystems. Reaction conditions are given in the text. The R(hyd) and R(MV) values are normalised to unit surface area of catalyst, calculated on the basis of spheres of radius r.

		Benzophenone			Zinc porphyrin		
x	r/nm	$R(H_2)$ /µmol min^{-1}	$[H_2]$ /mmol dm^{-3}	R(hyd) /µmol min^{-1}	$R(H_2)$ /µmol min^{-1}	$[H_2]$ /µmol dm^{-3}	R(MV) /µmol min^{-1}
0	0.8	3.05	65	42	1.70	60	98
6	1.2	2.35	58	27	2.05	70	31
12	1.5	2.32	54	14	2.25	75	11
20	2.6	2.26	42	5	2.55	96	3
35	4.7	1.97	36	2	2.30	140	1
50	6.8	1.10	20	<1	1.32	148	<1
100	14.5	0.06	2	<1	0.95	145	<1

performance of a catalyst can be improved markedly by forming an alloy with a compatible metal and it is known[4] that adding small amounts of Au to macroscopic Pt catalysts inhibits alkane hydrogenolysis whilst increasing the rate of dehydrogenation. Preliminary studies[5] have suggested that the same methodology can be applied to highly dispersed catalysts supported on graphite and we show here that bimetallic catalysts of colloidal dimensions have applications in solar energy storage devices operated under ambient conditions.

A series of colloidal dispersions of Pt and Au were prepared by γ-radiolysis[1,2] of mixtures of Na_2PtCl_6 and $NaAuCl_4$ in N_2-saturated water at pH 7 containing Carbowax 20 M (1×10^{-3} mol dm^{-3}). All solutions retained a total metal concentration of 5×10^{-4} mol dm^{-3} with the mole fraction of each metal varying from 0 to 1. The actual composition of each colloidal dispersion, after treatment with ion-exchange resins, was determined by atomic absorption and the average particle sizes were established by high-resolution transmission electron microscopy. The mixed Pt–Au colloids appear to be bimetallic particles,[5] not mixtures of discrete Pt and Au particles, since the average particle radius (r) increases smoothly with increasing mole fraction of Au (Table 1) with no indication of distributions of small and large particles within any single dispersion. X-Ray emission spectroscopy carried out in conjunction with scanning transmission electron microscopy confirmed that individual particles contained both Pt and Au but their relative intensities, compared to the atomic absorption results, suggested segregation with surface enrichment of Au.

The bimetallic colloids were used to catalyse H_2 evolution from well established sacrificial photosystems. In one set of experiments,[6] trimethylammonium 4-methylbenzophenone chloride (5×10^{-4} mol dm^{-3}) in N_2-saturated water at pH 7 containing ethanol (2% w/w) and colloid ([metal] = 2×10^{-4} mol dm^{-3}) was irradiated with UV light (λ 290 nm; 4×10^{18} photons min^{-1}). Evolution of H_2 was followed by gas chromatography as a function of irradiation time. It was found that both the maximum rate of evolution [$R(H_2)$], as observed during the initial stages of irradiation, and the maximum yield ($[H_2]$) of H_2, as obtained from exhaustive photolyses, decreased progressively with increasing mole fraction of Au (Table 1). In this system,[6] triplet state benzophenone abstracts a hydrogen atom from ethanol to form two ketyl radicals, both of which are highly reducing but short-lived owing to dimerisation and/or disproportionation reactions. The colloidal particles can intercept these bimolecular reactions and catalyse H_2 formation by functioning as microelectrodes.[1,2,7]

For a diffusion-controlled process, the efficiency with which a given concentration of colloid intercepts the bimolecular reactions and collects reducing equivalents from the ketyl radicals is inversely proportional to the square of the particle radius.[7] Consequently, larger particles are much less effective than their smaller counterparts. Increasing the mole fraction of Au has the effect of increasing the particle radius (Table 1) and, therefore, the bimetallic particles enriched in Au give lower $R(H_2)$ and $[H_2]$ values. For this system, where there are no thermodynamic restrictions and H_2 formation is controlled solely by kinetic factors,[7] the bimetallic colloids are less useful than the smaller colloids produced from pure Pt.

However, upon prolonged irradiation H_2 is consumed owing to hydrogenation of the carbonyl group and $[H_2]$ reaches an optimum value. This hydrogenation reaction was followed independently by bubbling H_2 through solutions of the benzophenone (5×10^{-4} mol dm^{-3}) in water at pH 7 containing colloid ([metal] = 2×10^{-4} mol dm^{-3}) at 70 °C. The course of reaction was followed by HPLC and the rates of hydrogenation [R(hyd)], corrected for variations in total surface area of the catalyst, were found to decrease markedly with increasing mole fraction of Au (Table 1). These results show clearly that colloidal Pt is a good catalyst for hydrogenation of benzophenone but even a low surface concentration of Au is sufficient to inhibit hydrogenation.

A second set of experiments[8] used zinc tetrakis(N-methyl-4-pyridinio)porphyrin (5×10^{-5} mol dm^{-3}) as photosensitiser, methyl viologen (1×10^{-3} mol dm^{-3}) (MV^{2+}) as electron relay, and dihydronicotinamide adenine dinucleotide (reduced form) (5×10^{-4} mol dm^{-3}) as sacrificial electron donor in N_2-saturated water at pH 4. This photosystem has no kinetic restrictions in that the reducing radical $MV^{\cdot +}$ is formed in high yield and persists for many hours in the absence of O_2, although the thermodynamics for H_2 evolution are less favourable than for the benzophenone system.[6—8] Photolysis (λ 555 nm, 3×10^{18} photons min^{-1}) in the presence of a colloid ([metal] 2×10^{-4} mol dm^{-3}) resulted in evolution of H_2 (Table 1). As the mole fraction of Au increases, there is an increase in $R(H_2)$ until an optimum value is reached at about 20—30% Au after which $R(H_2)$ decreases. There is also a progressive increase in $[H_2]$ as the mole fraction of Au increases (Table 1). Overall, the optimum composition for the catalyst appears to be about $Pt_{0.7}Au_{0.3}$.

The increased yields of H_2 obtained with increasing mole fraction of Au are attributed to inhibition of hydrogenation of the reactants by surface Au atoms. With mole fractions of Au exceeding 20%, H_2 is not consumed upon prolonged irradiation although this is a serious problem for colloids containing little or no Au. The effect of Au on the observed $R(H_2)$ values implies that many of the Pt atoms on the colloid surface are prevented from functioning as active catalytic H_2 evolving sites because of specific adsorption. The adsorbate may be evolving sites because of specific adsorption. The adsorbate may be $H^\cdot$ atoms, MV^{2+}, $MV^{\cdot+}$, or surfactant used to protect the colloid against flocculation. Incorporating Au atoms into the colloid surface dilutes Pt–Pt co-ordination sites where specific adsorption occurs, allowing surface Pt atoms to operate as active H_2 evolving sites. For mole fractions of Au exceeding 35%, and allowing for surface enrichment of Au, few Pt atoms will be resident at the colloid surface. This situation, although preventing specific adsorption, has a deleterious effect on $R(H_2)$ since the overpotential[9] for H_2 evolution on Au exceeds that on Pt. The thermodynamics for H_2 evolution with $MV^{\cdot+}$ as reducing agent at pH 4 are such that $R(H_2)$ will increase with decreasing overpotential.[8] Thus, the rate of H_2 formation shows an optimum mole fraction of Au.

In H_2-saturated aqueous solution at pH 4 containing colloidal Pt (2×10^{-4} mol dm^{-3}), the rates of hydrogenation of MV^{2+} and of the zinc porphyrin photosensitiser were too slow to be measured, even at 70 °C. In contrast, the reducing radical $MV^{\cdot+}$ is hydrogenated readily under ambient conditions and it is apparent that this reaction is responsible for consumption of H_2 during photolysis. The rate of hydrogenation of $MV^{\cdot+}$ [R(MV)], as catalysed by the various colloids, was measured by electrochemical methods. Thus, an Hg pool electrode was used to reduce MV^{2+} (1×10^{-4} mol dm^{-3}) in H_2-saturated water at pH 7 containing a colloid ([metal] 1×10^{-4} mol dm^{-3}). Aliquots of solution were removed periodically and aerated, and the concentration of MV^{2+} determined by HPLC. It was found that R(MV) decreased significantly with increasing mole fraction of Au (Table 1). The inhibition of hydrogenation of both benzophenone and $MV^{\cdot+}$ on the bimetallic particles is a consequence of several factors arising from electronic properties of the alloys, including decreased mobility of $H^\cdot$ atoms,[10] increased energy of adsorption of H_2,[11,12] and decreased specific adsorption of the reactants.[13]

This study has shown that, for photosystems not under kinetic control, the use of bimetallic Pt–Au colloids can give improved rates and yields of H_2 evolution. This arises because Au atoms at the surface of the colloidal particle inhibit specific adsorption and hydrogenation of the reactants. This behaviour, which is well known for macroscopic catalysts,[14,15] shows the advantages that may be gained by using alloys in place of pure metals. It is interesting to note that the performance of some of the bimetallic particles surpasses that of either of the pure metals. The situation, which should not be restricted to H_2 evolution, can be exploited to design new colloidal catalysts capable of improving the longevity of photochemical solar energy storage systems.

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